



Short communication

Influence of the solid electrolyte interphase on the performance of redox shuttle additives in Li-ion batteries – A rotating ring-disc electrode study

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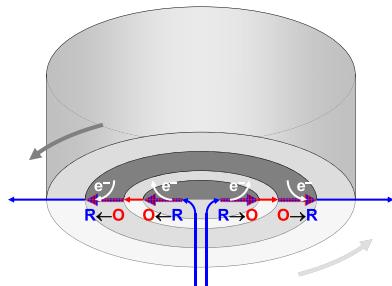
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HIGHLIGHTS

- The rotating ring-disc electrode is a powerful tool to study the reactions of redox shuttle additives.
- The presence of a SEI at the anode impedes the back-reduction of the RSA.
- The reduction behaviour of a RSA at the anode depends strongly on the characters of the RSA and the SEI.

GRAPHICAL ABSTRACT



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ABSTRACT

Redox shuttle electrolyte additives (RSAs) can be applied for reversible overcharge protection of batteries. Their successful operation involves their oxidation at the cathode and reduction at the anode. The most common anodes in lithium-ion batteries are graphite or amorphous carbon, which are normally covered with a solid electrolyte interphase (SEI). The reduction of RSAs at these anodes is in apparent contradiction with the common understanding of the SEI, which is thought to be electronically insulating. In this communication the reduction behaviour of ferrocene and 2,5-di-*tert*-butyl-1,4-dimethoxybenzene is studied at un-filmed and SEI-filmed electrodes. It is found that it depends strongly on the type of RSA and/or composition of the SEI. The rotating ring-disc electrode (RRDE) is introduced as a powerful diagnostic tool to study the reaction mechanism of RSAs in general and the influence of the SEI in particular.

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1. Introduction

Overcharge is an abuse condition which can shorten the cycle life of Li-ion batteries (LIBs) and lead to severe safety problems [1]. As an intrinsic way of protection against overcharge redox shuttle additives (RSAs) [2] have attracted widespread interest. RSAs can

readily be added to the electrolyte and are thus less complex to apply than other overcharge protection technologies, such as e.g. external voltage regulation [3,4]. Furthermore, RSAs provide reversible overcharge protection and the battery remains operative once the overcharge conditions are removed [5]. Several classes of molecules have been investigated for their applicability as RSAs (see for instance review [3] and the references given therein, and recent original research papers [6,7]). Among the very first molecules were ferrocene (Fc) and its derivatives [2,8,9]. Unfortunately, the redox potential of Fc of approx. 3.25 V vs. Li/Li⁺ is too low for

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any of the cathode materials which are used in LIBs today. For cells with LiFePO₄ as cathode 2,5-di-*tert*-butyl-1,4-dimethoxybenzene (DTBDMB) [10–12] appears especially promising.

The general working mechanism of a RSA comprises of four steps: (i) oxidation of the reduced form of the RSA (R) to the oxidised form of the RSA (O) at the cathode: R → O + e[−], (ii) diffusion of O from the cathode to the anode, (iii) back-reduction of O at the anode: O + e[−] → R, and (iv) diffusion of R from the anode to the cathode.

Relevant for a proper functioning are accordingly the redox potential, the reversibility of the redox process (including the stabilities of R and O), and kinetic parameters such as the diffusivities of R and O in the electrolyte. Information about these properties is commonly obtained by cyclic voltammetry (CV) or rotating disc electrode (RDE) voltammetry (e.g. Refs. [8,9,12]).

Step (iii) of the shuttle mechanism apparently contradicts the common understanding of state-of-the-art LIBs with graphite or amorphous carbon anodes, which are covered with a solid electrolyte interphase (SEI). The ideal SEI should behave like an electrolyte and be conductive for ions and insulating for electrons [13]. This raises the question how the RSA can gain electrons for the back-reduction at a SEI-filmed anode. This problem has been recognized and discussed before, e.g. by Moshurachak et al. [12] and Tang and Newman [14–16]. According to Moshurachak et al. the finding, that back-reduction of the RSA is possible even after the reduction of the electrolyte solution and SEI formation have come to an end, can be explained by differences in the electron tunnelling rate due to differences in energy of the final state (which is significantly lower for the oxidised RSA than for the solvent molecule or Li⁺ ion) [12].

Tang and Newman used ferrocene as probe to study the properties and growth of the SEI by RDE voltammetry [14]. They interpreted their results based on a two-layer SEI model with a compact inner layer and a porous outer layer, incorporating a previously proposed SEI growth model based on solvent transport through the SEI [17]. Electron tunnelling can occur across the inner layer, but it is impermeable for the RSA. The outer layer is beyond the electron tunnelling range, but it is porous enough to allow selective transport of the RSA through it. Their study showed that the reduction of ferrocenium (Fc⁺) is impeded by the presence of the SEI, and that the through-film reduction current can be approximately described by Butler-Volmer kinetics combined with a through-film limiting current [14].

Rotating ring-disc electrode (RRDE) voltammetry is a classical method for mechanistic and kinetic studies of electrochemical reactions. It has especially been used to investigate aqueous electrolyte systems (e.g. Ref. [18]) and lately also air electrodes in combination with non-aqueous electrolytes (e.g. Ref. [19]).

In the present work we introduce the RRDE as an ideal and powerful diagnostic tool to study the redox behaviour of RSAs. Ferrocene and DTBDMB were selected as model RSAs for the present RRDE study, since both are known to work reversibly, and since the results could be compared with the results from the previous studies mentioned above.

2. Experimental

The base electrolyte used in this study was 1 M LiPF₆ in ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 by wt.) from Ube Industries. Fc (98%) and DTBDMB (98%) were purchased from Sigma Aldrich and used without further purification.

Initial CV experiments in quiescent solution were carried out with a glassy carbon (GC) electrode (AFE2M050GC, Pine Research Instrumentation) with an area of 0.196 cm² and Li metal counter and reference electrodes using a scan rate of 10 mV s^{−1}.

The RRDE experiments were performed with a GC ring – GC disc electrode (custom-manufactured by Pine Research Instrumentation) with a ring area of 0.187 cm², a disc area of 0.247 cm², a ring-disc distance of 320 μm, and a theoretical collection efficiency (η_{theo}) of 0.371. The RRDE was polished with a 0.05 μm diamond suspension (Buehler) prior to each set of experiments. All experiments were performed in a glove-box with Ar atmosphere and oxygen and water levels <1 ppm at a temperature of 24 ± 2 °C. Lithium metal served as reference and counter electrodes. The rotation speed of the ring-disc electrode was controlled by a rotator (Model 636A, Princeton Applied Research) between 200 and 2400 rpm. The electrochemical measurements were performed with 2 potentiostats (Versastat 4 and Versastat 3F, Princeton Applied Research) in bipotentiostat mode. The disc potential was linearly swept from an initial to a final potential at 10 mV s^{−1}, meanwhile the ring potential was kept at a constant potential and the current was recorded as a function of time. Apparent collection efficiencies (η_{app}) were calculated from the ratio of ring current (I_{ring}) to disc current (I_{disc}) using measured values from the limiting current regions [20]:

$$\eta_{\text{app}} = \frac{I_{\text{ring}}}{I_{\text{disc}}} \quad (1)$$

The concentration of RSA used in the CV and RRDE experiments was 0.01 M or 0.05 M and thus well below the solubility limits of DTBDMB (approx. 0.06 M) and ferrocene (at least 0.5 M) in the present base electrolyte. Both the CV and RRDE experiments were carried out without IR compensation.

SEI-prefilming of the ring electrode was performed by running 3 CV cycles in quiescent solution between 1.5 and 0.02 V vs. Li/Li⁺ (starting at OCV) at 1 mV s^{−1}.

3. Results and discussion

3.1. CV measurements

Initially, ferrocene and DTBDMC were studied by CV in quiescent solution. The CV curves for 0.01 M ferrocene and 0.01 M DTBDMB in 1 M LiPF₆/EC:DMC (1:1 by wt.) are presented in Fig. 1 and reflect the reversible redox behaviours of these two molecules. The mid-peak potentials [$E_{\text{mp}} = (E_{\text{pa}} + E_{\text{pc}})/2$] and the peak difference values ($\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$) were obtained as $E_{\text{mp}}(\text{Fc}/\text{Fc}^+) = 3.24$ V vs. Li/Li⁺, $E_{\text{mp}}(\text{DTBDMB}/\text{DTBDMB}^{*+}) = 3.93$ V vs. Li/Li⁺, $\Delta E_p(\text{Fc}/\text{Fc}^+) = 81$ mV, and $\Delta E_p(\text{DTBDMB}/\text{DTBDMB}^{*+}) = 79$ mV, with E_{pa} and E_{pc} denoting

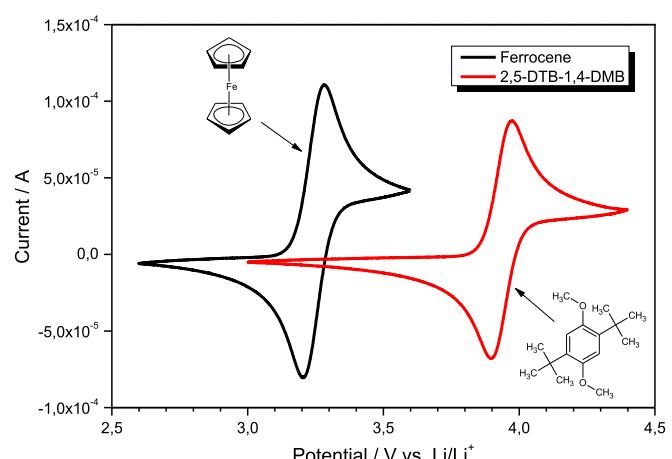


Fig. 1. Cyclic voltammograms of 0.01 M ferrocene and 0.01 M DTBDMB in 1 M LiPF₆/EC:DMC (1:1 by wt.) on a GC electrode at 10 mV s^{−1} (in quiescent solution).

the peak potentials of the anodic and cathodic waves. These results compare well with previously reported data [8,9,11–14,21].

3.2. RRDE measurements with un-filmed ring electrode

The RRDE allows studying two electrochemical reactions simultaneously. In the case of RSAs the basic idea is to oxidise the reduced version of the RSA (R) at the disc electrode and to simultaneously study the back-reduction of the oxidised version of the RSA (O) at the ring electrode. Experimentally this was realised by sweeping the potential of the disc electrode at a scan rate of 10 mV s^{-1} from values below to values above the redox potential of the RSA (from 2.5 to 4.5 V vs. Li/Li⁺ for ferrocene and from 3.0 to 4.5 V vs. Li/Li⁺ for DTBDMB) while keeping the ring potential at a constant value well below the redox potential (2.5 V vs. Li/Li⁺ for ferrocene and 3.0 V vs. Li/Li⁺ DTBDMB). The current vs. time curves recorded at the disc and ring electrodes at different rotation speeds are shown in Figs. 2a and 3a.

The limiting current regions were reached at around 3.5 and 4.0 V vs. Li/Li⁺ and data were read at 175 and 130 s after the start of the measurement for ferrocene and DTBDMB, respectively. The apparent collection efficiencies (η_{app}), as calculated from the limiting currents, are listed in Table 1. For ferrocene values between 0.38 and 0.39 were obtained, which correspond well to $\eta_{\text{theo}} = 0.37$ of the electrode within the experimental uncertainties. For DTBDMB the values were even slightly higher, between 0.39 and 0.40. This can probably be explained with the onset of a second oxidation step followed by irreversible decomposition reactions above 4.4 V vs. Li/Li⁺ [21], which then cause additional reduction reactions which increase the cathodic base current. In summary, in the case of the un-filmed ring electrode (anode) the oxidation/reduction process is essentially reversible and the back-reduction is not kinetically hindered for both RSAs.

3.3. RRDE measurements with pre-filmed ring electrode

The first experiment to test for the reversibility of the redox process of a RSA is usually to perform CV at unfilmed electrodes. In a real LIB, however, the back-reduction occurs at the anode in the cell. For graphite, as the most common anode, the working potential is around 100–300 mV vs. Li/Li⁺ and the anode will be filmed with a SEI, which will influence the back-reduction of the RSA. The RRDE allows simulating this situation. The ring electrode can be covered with a SEI, and the back-reduction of O can be measured in the presence of this SEI. GC was selected as RRDE electrode material (rather than other, more commonly used materials such as Pt) in order to mimic the typical carbon surface chemistry of graphite anodes as close as possible. (It has been shown before, e.g. by FTIR spectroscopy [22], that the SEI-films on GC and graphite are in a first approximation rather similar, although more detailed investigations indicate that the exact composition and thickness depends on the specific type of carbon material [23].)

In the present study the SEI formation was realised by carrying out 3 CV cycles at 1 mV s^{-1} directly in the RSA-containing electrolyte (Figs. 2b and 3b). Afterwards, the filmed-ring and disc electrode assembly was directly used for the same set of experiments as before.

The results for ferrocene are shown in Fig. 2c. The linear sweep voltammograms at the disc electrode are identical to those in Fig. 2a, which is in accordance with the fact, that the experimental conditions at the disc electrode are identical. Instead, a significant change is observed for the ring currents, which declined 4 orders of magnitude compared to those obtained with the un-filmed ring electrode (Table 1) and were close to the background current (note

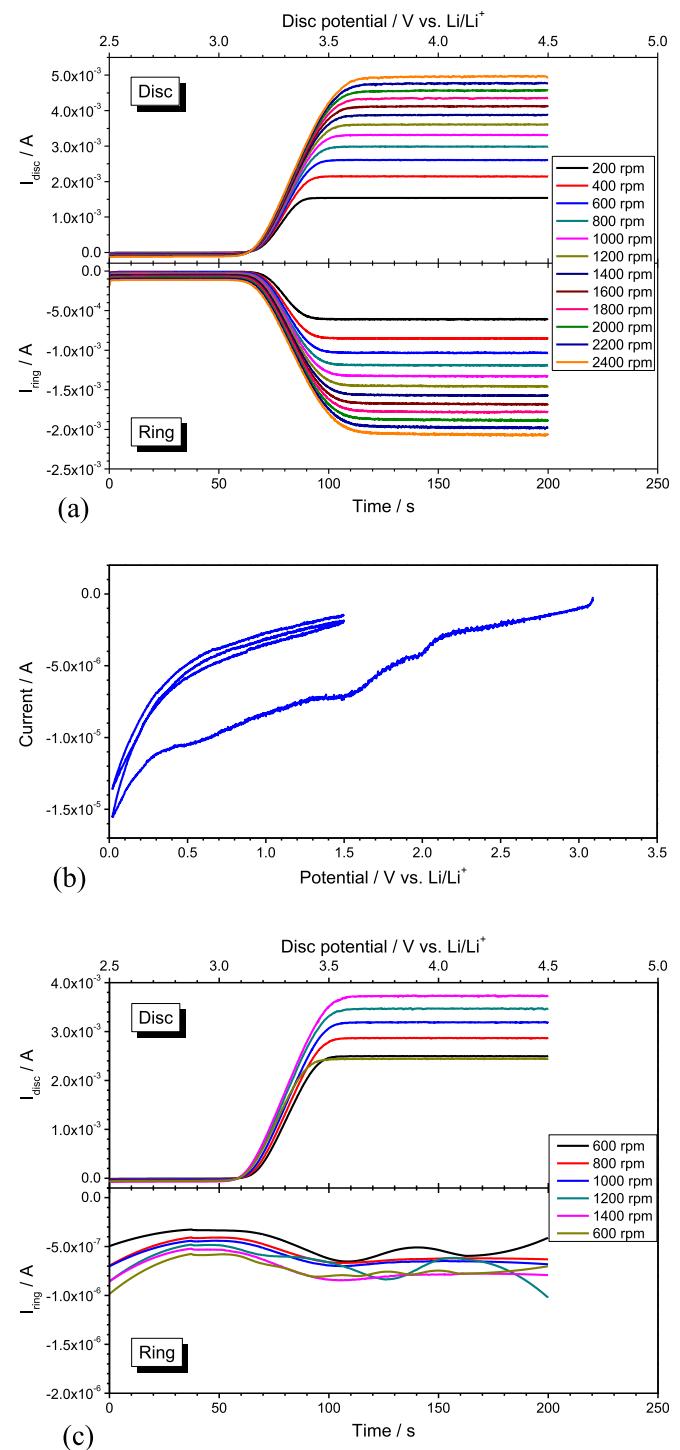


Fig. 2. RRDE measurements for 0.05 M ferrocene in 1 M LiPF₆/EC:DMC (1:1 by wt.). (a) Un-filmed ring electrode, (b) pre-filming of ring electrode, (c) filmed ring electrode. (see Table 1 for the sequence of rotation speeds in (a) and (c)).

that the ring currents in Fig. 2c were smoothed). Obviously, in the case of ferrocene (and a SEI formed in the presence of ferrocene) the back-reduction of Fc^+ is almost completely blocked. Within the framework of the 2-layer SEI model [14–16] and assuming that the critical step is the diffusion of O through the porous outer part of the SEI, this can be interpreted such that Fc^+ can hardly move through the SEI (or that the SEI formed in the presence of ferrocene is too dense to allow the transport of Fc^+).

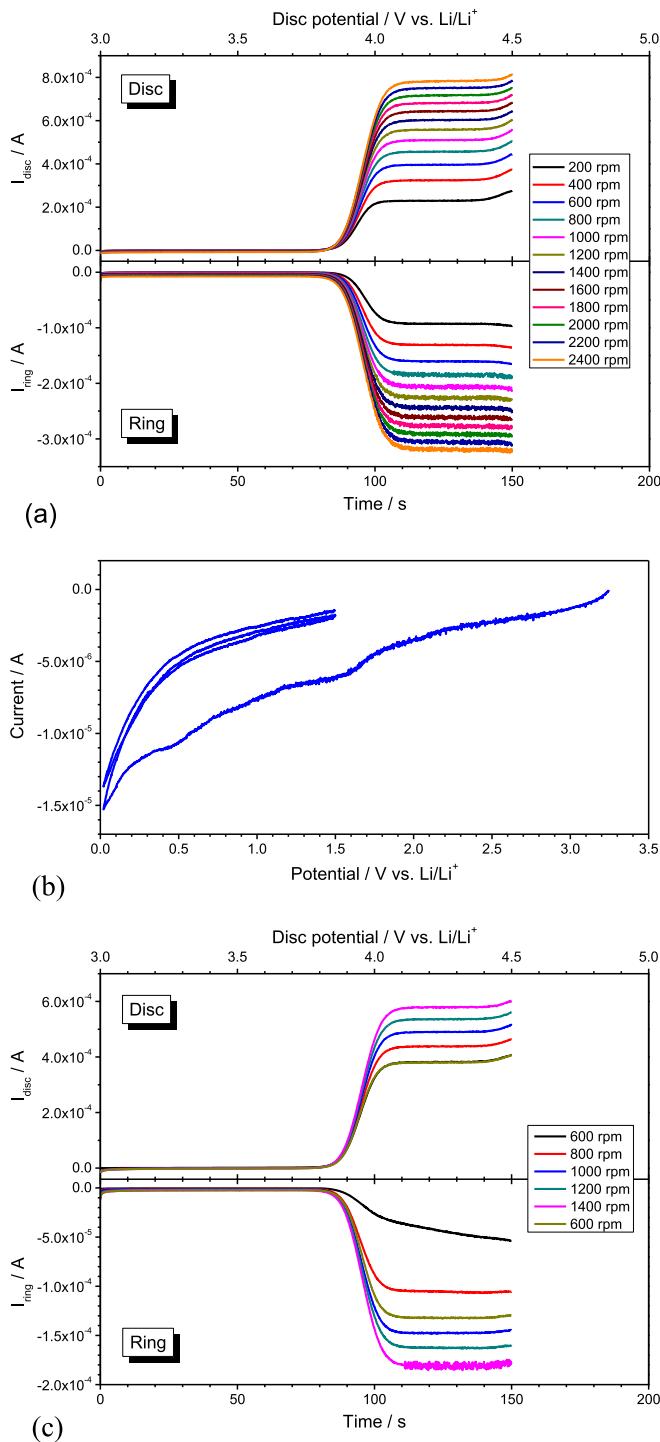


Fig. 3. RRDE measurements for 0.01 M DTBDMB in 1 M LiPF₆/EC:DMC (1:1 by wt.). (a) Un-filmed ring electrode, (b) pre-filming of ring electrode, (c) filmed ring electrode. (see Table 1 for the sequence of rotation speeds in (a) and (c)).

Fig. 3c presents the results for DTBDMB. Again, the signals observed at the disc electrode are equal to those in **Fig. 3a** and the signals observed at the filmed ring electrode are lower than for the un-filmed ring electrode. The blocking of the back-reduction is, however, much less pronounced than in the case of ferrocene and values of η_{app} between 0.12 and 0.34 (corresponding to 32–92% of η_{theo}) are observed. This means that in the case of DTBDMB (and a SEI formed in the presence of DTBDMB) back-reduction remains

Table 1
Apparent collection efficiencies derived from Figs. 2 and 3.

Rotation speed/rpm	Apparent collection efficiency η_{app}			
	Un-filmed ring electrode		Filmed ring electrode	
	Ferrocene (Fig. 2a)	DTBDMB (Fig. 3a)	Ferrocene (Fig. 2c)	DTBDMB (Fig. 3c)
200	0.39	0.40		
400	0.39	0.41		
600	0.38	0.40	1.0×10^{-4}	0.12
800	0.39	0.40	7.3×10^{-5}	0.24
1000	0.39	0.40	6.8×10^{-5}	0.30
1200	0.39	0.40	7.1×10^{-5}	0.30
1400	0.39	0.40	6.5×10^{-5}	0.31
1600	0.38	0.39		
1800	0.39	0.40		
2000	0.38	0.39		
2200	0.39	0.39		
2400	0.39	0.39		
600			7.4×10^{-5}	0.34

possible – though at a lower level than on an un-filmed electrode. Accordingly, a better overcharge performance can be expected for DTBDMB than for ferrocene.

For DTBDMB η_{app} seems to increase with increasing rotation speed. However, it has to be considered that the electrode rotation during the experiments exerts considerable mechanical stress on the SEI film at the ring electrode, and that it cannot be excluded that parts of the film are sheathed off the electrode by the electrolyte flow induced by the electrode rotation. To check for this effect the last rotation speed in the series of measurements was set equal to the first one (i.e. 600 rpm). As seen in Table 1 η_{app} increased from 0.12 to 0.34 from the beginning to the end of the measurement series, which indicates that in the case of DTBDMB the SEI was not mechanically stable and was partly removed. Hence the initial value for η_{app} has to be considered as the value which is closer to reality.

Interestingly, for ferrocene η_{app} does not change with time, and the SEI formed in the presence of ferrocene appears more stable than that formed in the presence of DTBDMB.

4. Conclusions

A RRDE has been used to study the operation mechanism of RSAs for the first time. It is shown that even if the redox process is in principle reversible, the presence of a SEI impedes the back-reduction of the RSA at the anode and will thus affect the operation of the RSA in a full cell. The actual reduction behaviour at the anode depends strongly on the type of RSA and the character of the SEI (in accordance with Ref. [14]).

The great advantage of the RRDE over a RDE (as used in Ref. [14]) is that it allows studying oxidation and reduction of the RSA simultaneously, by performing oxidation of R at the disc electrode and reduction of O at the ring electrode. Therefore, both the reversibility of the redox process and the influence of the SEI on the RSA reduction can be investigated. For the study of the reduction process of O with a RDE it is furthermore necessary that the electrolyte already contains O. Hence O has to be added to the electrolyte (which is possible for Fc^+ , which is commercially available, but may be impossible for other RSAs, which are not available in the oxidised form) or to be electrochemically produced from R by oxidation prior to the measurement. The RRDE instead allows generating O *in situ* from R.

The full potential of RRDE voltammetry will be demonstrated in a forthcoming paper with a detailed study on several RSAs in combination with SEIs formed in different electrolyte solutions [24].

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